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⑤④ **Method of heterogeneous reaction.**

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⑦③ Proprietor: **NIPPON OIL AND FATS COMPANY,**  
**LIMITED**  
**10-1, Yuraku-cho 1-chome**  
**Chiyoda-ku Tokyo (JP)**

⑦② Inventor: **Funada, Tadashi**  
**No. 2-53-1-104, Mukonosounishi**  
**Amagasaki-shi Hyogo (JP)**  
Inventor: **Hirano, Jiro**  
**No. 2340-9, Akuwa-cho Seya-ku**  
**Yokohama-shi Kanagawa (JP)**  
Inventor: **Ishida, Shiro**  
**No. 1-17-24, Hikarigaoka**  
**Takarazuka-shi Hyogo (JP)**  
Inventor: **Morioka, Kensuke**  
**No. 23, Matsuuchi-cho**  
**Amasaki-shi Hyogo (JP)**  
Inventor: **Murakami, Sachiko**  
**No. 3-15-9, Nakakosaka**  
**Higashi-Osaka-shi Osaka (JP)**

⑦④ Representative: **Hansen, Bernd, Dr.rer.nat. et al**  
**Hoffmann, Eitle & Partner Patentanwälte**  
**Arabellastrasse 4**  
**D-8000 München 81 (DE)**

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**EP 0 121 265 B1**

**Description**

The present invention relates to a method of carrying out a heterogeneous reaction and more particularly to a method of reacting an oil-soluble component with a water-soluble component in a heterogeneous system.

In the heterogeneous reaction of an oil-soluble component with a water-soluble component, a stirring method using power, an emulsification method using surface active agents, a critical reaction method under high-temperature and high-pressure conditions, and so forth have heretofore been employed in order to obtain uniform mixing of the reactants. These methods, however, have various disadvantages, such as consumption of significant energy for the stirring operation or for maintaining high-temperature and high-pressure conditions, danger involved in realizing the high-temperature and high-pressure conditions, and a need to break emulsions after the completion of the reaction.

European patent application EP—A—120285, published 3.10.84 and being prior art in the meaning of art 54.3 and 54.4 EPC, describes a biochemical process comprising reacting an (a) hydrophobic substrate with (b) a solution or dispersion comprising a hydrophilic substrate and enzyme catalyst, by contacting said hydrophilic substrate and said hydrophobic substrate through a porous thin membrane, wherein said hydrophilic substrate and said hydrophobic substrate are incompatible with each other. In this process the two substrates remain separated from each other by the thin membrane.

The invention comprises a method of carrying out a heterogeneous reaction, wherein an oil-soluble component is dispersed in a water-soluble component or in its aqueous solution and is reacted with the water-soluble component, and is characterized in that the oil-soluble component is dispersed by passing it through micropores of a disperser fabricated from a hydrophilic material as it enters the water-soluble component or its aqueous solution.

In accordance with the present invention, a column, for example, is filled with a water-soluble component or its aqueous solution, and an oil-soluble component is introduced into the column from either the top thereof or the bottom depending on the specific gravity thereof, in a manner so that the oil-soluble component enters into the water-soluble component or is its aqueous solution in a dispersed form. For this, the oil-soluble component is introduced into the water-soluble component or its aqueous solution through a dispersion apparatus (hereinafter referred merely as a "disperser") made of a hydrophilic material having micropores and as a result passes through the water-soluble component or its aqueous solution in the form of fine, minute droplets.

Hydrophilic materials which can be used in the fabrication of the disperser as used herein include hydrophilic organic materials such as polyvinyl alcohol, polyvinyl formal, polyvinyl acetic acetal, polyvinyl acetal, cellulose, acetyl cellulose, nitro cellulose, acetyl butyl cellulose, ethyl cellulose, methyl cellulose, benzyl cellulose, polypeptide, agar, carrageenan or gelatin; hydrophilic inorganic materials such as glass, gypsum, cement, alumina, silica gel or asbest; natural fibers such as cotton, kapok, linen, ramie, hemp, jute, Manila hemp, sisal, New Zealand hemp, coir, mohair, cashmere, goat hair, camel hair, vicuna wool, alpaca hair, lama hair, horse hair or silk; and manufactured fibers such as viscose rayon, cuprammonium rayon, polynosic rayon or casein. These hydrophilic materials can be used in admixture with lipophilic materials, or in a state that they are attached onto the surface of lipophilic materials.

The disperser as used herein may be fabricated in various forms such as membrane, or plate, or gel or other layer-formed structure made of the hydrophilic material described above, or in the form of an interwoven or knit fabric (constructed fabric) or non-woven fabric structure made of threads of the hydrophilic material. It is preferred for the disperser to have micropores having a diameter of from 0.005 to 5 mm, more preferably from 0.01 to 1 mm. The oil-soluble component is dispersed into the water-soluble component or its aqueous solution by means of the above-described disperser and then is allowed to rise or fall through the water-soluble component or its aqueous solution owing to a sufficient difference in specific gravity between the two components.

The invention comprises a heterogeneous reaction, wherein the reaction product is a liquid immiscible with the water-soluble component or its aqueous solution, or precipitates therein, and also a heterogeneous reaction, wherein the reaction product floats on the surface of the water-soluble component or its aqueous solution, and a heterogeneous reaction, wherein the reaction product is recycled.

With regard to conditions under which the method of the present invention is carried out, the temperature, pressure and so forth can be appropriately determined depending on the disperser, column, reaction materials, catalyst, and so forth. The reaction temperature is usually from 10 to 150°C, and the reaction pressure may be atmospheric, sub-atmospheric or superatmospheric pressure. A catalyst can be used in the following manner: it is dissolved in any one of the water-soluble component and the oil-soluble component, or in the case of an insoluble catalyst such as a solid catalyst and a catalyst adsorbed or immobilized onto a support, it is packed in the column, singly or in combination with a packed material, so that it can easily come into contact with the reaction materials.

The water-soluble component as used herein includes substances such as water, methyl alcohol, ethyl alcohol, ethylene glycol, propylene glycol, glycerol, neopentyl polyol, sugar, glucose, and sorbitol and aqueous solutions of various other organic or inorganic substances such as monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, triisopropanolamine, ammonia, hydrogen peroxide, bromine, iodine, hydrochloric acid, hydrobromic acid, hydroiodic acid,

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sulfuric acid or nitric acid. The oil-soluble components includes aliphatic carboxylic acids having at least 6 carbon atoms, aliphatic hydrocarbons having at least 6 carbon atoms, aromatic compounds containing at least 6 carbon atoms, natural animal or vegetable oils and fats, and various synthetic glycerides. In addition, esters such as methyl oleate, methyl palmitate, ethyl stearate, oleyl oleate, sorbitan trioleate, and sucrose fatty acid esters can be used.

It should be noted that the above-stated examples of oil-soluble and water-soluble reaction components are presented for exemplification only and the skilled artisan will be able to readily select other reactive components to be used in the heterogeneous reaction system disclosed herein, for example, the many different types of reactants which can participate in the types of heterogeneous reactions disclosed hereinbelow.

The method of the present invention produces various advantages. For example, since the particle size of the oil-soluble component can be controlled by means of the disperser made of the hydrophilic material, the flow rate, reaction rate, and conversion are easy to control. Furthermore, since the method of the present invention does not need stirring power nor an emulsification operation, and further can be performed continuously, it can be suitably used in a wide variety of heterogeneous reactions utilizing an oil-soluble component and water-soluble component, such as esterification, ester exchange, hydrolysis, oxidation, reduction and addition.

Usually, in the practice of the present invention, the size of the oil droplets as introduced into the water-soluble component or its aqueous solution is about 0.005 to 5 mm, preferably about 0.01 to 1 mm and, most of the oil droplets stay about the same size during the reaction.

The present invention is described in detail with reference to the following examples.

### Example 1

Glycerol containing 2% by weight of sulfuric acid was used to fill a cylindrical glass vessel (height: 100 cm; inner diameter: 3 cm) and was maintained at 150°C. Fifty grams of oleic acid (purity: 99%) was introduced into the vessel from the bottom thereof through a 5 mm thick gypsum plate having a number of micropores of diameter of about 0.3 mm in the form of oil droplets having a particle size of from 0.5 to 1 mm, and was allowed to rise through the vessel at a space velocity of  $5.7 \times 10^{-2} \text{hr}^{-1}$ . An esterification reaction occurred between the glycerol and oleic acid. The reaction product, which floated on the top of the reaction mixture, was recycled. The reaction was carried out for 200 minutes (the reaction product was recycled 10 times). The conversion of esterification as determined by the equation as described below was 90%.

$$\text{Conversion of Esterification} = \frac{\text{Acid value before reaction} - \text{Acid value after reaction}}{\text{Acid value before reaction}} \times 100$$

### Comparative Example 1

Fifty grams of glycerol containing 2% by weight of sulfuric acid and 50 g of oleic acid (purity: 99%) were placed in a 300 ml flask and esterified at 130°C while stirring. The time required until the conversion of esterification reached 90% was 350 minutes, which is about 1.8 times that of Example 1. That is, in this example, the time as long as about 1.8 times that of Example 1 was needed to attain the same conversion of esterification as in Example 1.

### Example 2

Methyl alcohol containing 2% by weight of potassium hydroxide was used to fill the same cylindrical vessel as used in Example 1 and was maintained at 45—50°C. Olive oil (acid value: 0.3; saponification value: 192) was introduced into the vessel from the top thereof through an about 2 mm thick cotton fabric in the form of oil droplets having a particle size of from 0.5 to 0.7 mm and was allowed to fall at a space velocity of  $5.7 \times 10^{-2} \text{hr}^{-1}$ . The methyl alcohol and olive oil reacted with one another. The reaction product precipitated and was recycled 6 times. Gas chromatography analysis showed that 90% of the olive oil was converted into the fatty acid methyl ester thereof.

### Example 3

The procedure of Example 2 was repeated wherein the cotton fabric was replaced by an about 1 mm thick acetyl cellulose membrane having a number of micropores of diameter 0.05—0.1 mm. The particle size of the oil droplets was 0.3—0.5 mm and the space velocity was  $3.5 \times 10^{-2} \text{hr}^{-1}$ . The reaction product was recycled four times. The yield of fatty acid methyl ester was 95%.

### Example 4

An aqueous lipase solution (500 unit/ml) was used to fill the same cylindrical vessel as used in Example 1 and was maintained at 35°C. Olive oil (acid value: 0.3; saponification value: 192) was introduced into the vessel from the bottom thereof through a 1 cm thick agar gel having a number of micropores of diameter about 0.2 mm in the form of oil droplets having a diameter of 0.3—0.5 mm, and was allowed to rise through the vessel at a space velocity of  $4.5 \times 10^{-2} \text{hr}^{-1}$ , whereby the olive oil and the water reacted with one another

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using the lipase. The reaction product, found floating on the top of the reaction mixture, was recycled. After the reaction product was recycled seven times, the conversion of hydrolysis was 93%.

$$\text{Conversion of hydrolysis} = \frac{\text{Acid value}}{\text{Saponification value}} \times 100$$

### Example 5

The procedure of Example 4 was repeated except the agar gel was replaced by an about 2 mm thick alumina plate having a number of micropores of diameter 0.15—0.2 mm and an aqueous lipase solution (1,000 unit/ml) was used. The particle size of the oil droplets was 0.2—0.3 mm and the space velocity was  $4 \times 10^{-2} \text{hr}^{-1}$ .

The reaction product was recycled five times. The conversion of hydrolysis of olive oil was 95%.

### Example 6

A cylindrical vessel (height: 150 mm; inner diameter: 15 mm) was charged with 25 ml of an immobilized enzyme prepared by adsorbing 0.1 g of lipase onto oxirane-acrylic beads (produced by Röhm Pharma GMBH, West Germany) and water. Olive oil was introduced into the vessel from the bottom thereof through the same cotton fabric as used in Example 2 and was allowed to rise through the vessel at a space velocity of  $2 \times 10^{-3} \text{hr}^{-1}$ .

The reaction product was recycled 30 times. The conversion of hydrolysis of olive oil was 60%.

### Example 7

A fermentation broth obtained by cultivating a strain belonging to the genus *Corynebacterium* and having an  $\omega$ -oxidation activity was subjected to a ultrasonic wave treatment to break the cells, diluted two-fold with deionized water, placed in the same cylindrical vessel as used in Example 1, and maintained at 35°C. n-Decane was introduced into the vessel from the bottom thereof through a fabric of hemp in the form of oil droplets having a diameter of 0.3—0.5 mm and was allowed to rise at a space velocity of  $4.5 \times 10^{-2} \text{hr}^{-1}$  to cause the  $\omega$ -oxidation reaction. The reaction product, found floating on the top of the reaction mixture, was recycled. After the reaction product was recycled 10 times, the oxidized n-decane had an acid value of 15.

From the above description it is apparent that the stationary water-soluble phase can take various forms, in which the reactive component can be dissolved within the aqueous phase or be the aqueous phase itself.

Variations of the above examples will be apparent to the skilled artisan without departing from the concept of the invention as defined in the claims. For example, the vessel containing the water-soluble component need not be vertically-positioned as long as top-to-bottom or bottom-to-top flow of the dispersed oil-soluble component can occur.

## Claims

1. A method of carrying out a heterogeneous reaction, wherein an oil-soluble component is dispersed in a water-soluble component or in its aqueous solution and is reacted with the water-soluble component, characterized in that the oil-soluble component is dispersed by passing it through micropores of a disperser fabricated from a hydrophilic material as it enters the water-soluble component or its aqueous solution.

2. The method of heterogeneous reaction as claimed in claim 1, wherein the disperser is fabricated in a form of a membrane, a gel, a plate, another layer-formed structure, a constructed fabric or a non-woven fabric.

3. The method of heterogeneous reaction as claimed in claim 1, wherein the micropores have a diameter of from 0.005 to 5 mm.

4. The method of heterogeneous reaction as claimed in claim 3, wherein the micropores have a diameter of from 0.01 to 1 mm.

5. The method of heterogeneous reaction as claimed in Claim 1, wherein the hydrophilic material is a hydrophilic organic material, a hydrophilic inorganic material, a natural fiber or a manufactured fiber.

6. The method of heterogeneous reaction as claimed in Claim 5, wherein the hydrophilic organic material is polyvinyl alcohol, polyvinyl formal, polyvinyl acetic acetal, polyvinyl acetal, cellulose, acetyl cellulose, nitro cellulose, acetyl butyl cellulose, ethyl cellulose, methyl cellulose, benzyl cellulose, polypeptide, agar, carrageenan, or gelatin.

7. The method of heterogeneous reaction as claimed in Claim 5, wherein the hydrophilic inorganic material is glass, gypsum, cement, alumina, silica gel, or asbest.

8. The method of heterogeneous reaction as claimed in Claim 5, wherein the natural fiber is cotton, kapok, linen, ramie, jute, Manila hemp, sisal, New Zealand hemp, coir, mohair, cashmere, goat hair, camel hair, vicuna wool, alpaca hair, lama hair, horse hair or silk.

9. The method of heterogeneous reaction as claimed in Claim 5, wherein the manufactured fiber is viscose rayon, cuprammonium rayon, polynosic rayon or casein.

10. The method of heterogeneous reaction as claimed in Claim 1, wherein the water-soluble component is water, methyl alcohol, ethyl alcohol, ethylene glycol, propylene glycol, glycerol, neopentyl polyol, sugar, glucose or sorbitol.

11. The method of heterogeneous reaction as claimed in Claim 1, wherein the oil-soluble component is an aliphatic carboxylic acid having at least 6 carbon atoms, an aliphatic hydrocarbon having at least 6 carbon atoms, an aromatic compound having at least 6 carbon atoms, natural animal or vegetable oils and fats, synthetic glycerides, or an ester.

12. The method of heterogeneous reaction as claimed in Claim 11, wherein the ester is methyl oleate, methyl palmitate, ethyl stearate, oleyl oleate, sorbitan trioleate, or sucrose fatty acid ester.

13. The method of heterogeneous reaction as claimed in Claim 1, wherein the water-soluble component or its aqueous solution and the oil-soluble component differ sufficiently in specific gravity so that the oil-soluble component will rise or fall through the water-soluble component or its aqueous solution.

14. The method of heterogeneous reaction as claimed in Claim 13, wherein the water-soluble component or its aqueous solution is contained within a vessel and the oil-soluble component passes through the hydrophilic material positioned at the top or the bottom of the vessel.

15. The method of heterogeneous reaction as claimed in Claim 13, wherein the reaction product is a liquid immiscible with the water-soluble component or its aqueous solution, or precipitates therein.

16. The method of heterogeneous reaction as claimed in Claim 14, wherein the reaction product floats on the surface of the water-soluble component or its aqueous solution.

17. The method of heterogeneous reaction as claimed in Claim 15, wherein the reaction product is recycled.

18. The method of heterogeneous reaction as claimed in Claim 16, wherein the reaction product is recycled.

19. The method of heterogeneous reaction as claimed in Claim 13, wherein the reaction product is recycled.

### 30 Patentansprüche

1. Verfahren zum Durchführen einer heterogenen Reaktion, bei dem eine öllösliche Komponente in einer wasserlöslichen Komponente oder in deren wäßriger Lösung dispergiert und mit der wasserlöslichen Komponente umgesetzt wird, dadurch gekennzeichnet, daß man die öllösliche Komponente dispergiert, indem man sie durch Mikroporen eines aus einem hydrophilen Material hergestellten Dispergators beim Eintritt in die wasserlösliche Komponente oder deren wäßrige Lösung leitet.

2. Heterogenes Reaktionsverfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß der Dispergator aus einer Membran, einem Gel, einer Platte, einer anderen Schichtstruktur, einem Gewebe oder einem Vlies hergestellt ist.

3. Heterogenes Reaktionsverfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß die Mikroporen einen Durchmesser von 0,005 bis 5 mm haben.

4. Heterogenes Reaktionsverfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß die Mikroporen einen Durchmesser von 0,01 bis 1 mm haben.

5. Heterogenes Reaktionsverfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß das hydrophile Material ein hydrophiles organisches Material, ein hydrophiles anorganisches Material, eine Naturfaser oder eine Kunstfaser ist.

6. Heterogenes Reaktionsverfahren gemäß Anspruch 5, dadurch gekennzeichnet, daß das hydrophile organische Material Polyvinylalkohol, Polyvinylformal, Polyvinylelessigsäureacetal, Polyvinylacetal, Cellulose, Acetylcellulose, Nitrocellulose, Acetylbutylcellulose, Ethylcellulose, Methylcellulose, Benzylcellulose, Polypeptid, Agar, Carragenan oder Gelatine ist.

7. Heterogenes Reaktionsverfahren gemäß Anspruch 5, dadurch gekennzeichnet, daß das hydrophile anorganische Material Glas, Gips, Zement, Aluminiumoxid, Kieselgel oder Asbest ist.

8. Heterogenes Reaktionsverfahren gemäß Anspruch 5, dadurch gekennzeichnet, daß die Naturfaser Baumwolle, Kapok, Leinen, Ramie, Jute, Manila-Hanf, Sisal, Neu-Seeland-Hanf, Kokusfaser, Mohair, Cashmere, Ziegenhaar, Kamelhaar, Vicunawolle, Alpakahaar, Lamahaar, Pferdehaar oder Seide ist.

9. Heterogenes Reaktionsverfahren gemäß Anspruch 5, dadurch gekennzeichnet, daß die Kunstfaser Viskoserayon, Kupferammoniumrayon, Polynoserayon oder Kasein ist.

10. Heterogenes Reaktionsverfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß die wasserlösliche Komponente Wasser, Methylalkohol, Ethylalkohol, Ethylenglykol, Propylenglykol, Glycerin, Neopentylpolyol, Zucker, Glukose oder Sorbit ist.

11. Heterogenes Reaktionsverfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß die öllösliche Komponente eine aliphatische Carboxylsäure mit wenigstens 6 Kohlenstoffatomen, ein aliphatischer Kohlenwasserstoff mit wenigstens 6 Kohlenstoffatome, eine aromatische Verbindung mit wenigstens 6 Kohlenstoffatomen, ein natürliches tierisches oder pflanzliches Öl oder Fett, ein synthetisches Glycerid oder ein Ester ist.

12. Heterogenes Reaktionsverfahren gemäß Anspruch 11, dadurch gekennzeichnet, daß der Ester Methyloleat, Methylpalmitat, Ethylstearat, Oleyloleat, Sorbittrioleat oder Saccharosefettsäureester ist.

13. Heterogenes Reaktionsverfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß die wasserlösliche Komponente oder deren wäßrige Lösung und die öllösliche Komponente sich ausreichend  
5 in ihrem spezifischen Gewicht unterscheiden, so daß die öllösliche Komponente durch die wasserlösliche Komponente oder deren wäßrige Lösung aufsteigt oder fällt.

14. Heterogenes Reaktionsverfahren gemäß Anspruch 13, dadurch gekennzeichnet, daß die wasserlösliche Komponente oder deren wäßrige Lösung sich in einem Gefäß befindet, und die öllösliche Komponente durch das hydrophile Material, das sich am oberen Teil oder am Boden des Gefäßes  
10 befindet, hindurchgeht.

15. Heterogenes Reaktionsverfahren gemäß Anspruch 13, dadurch gekennzeichnet, daß das Reaktionsprodukt eine Flüssigkeit ist, die mit der wasserlöslichen Komponente oder deren wäßriger Lösung unmischar ist, oder darin ausfällt.

16. Heterogenes Reaktionsverfahren gemäß Anspruch 14, dadurch gekennzeichnet, daß das Reaktions-  
15 produkt an der Oberfläche der wasserlöslichen Komponente oder deren wäßriger Lösung schwimmt.

17. Heterogenes Reaktionsverfahren gemäß Anspruch 15, dadurch gekennzeichnet, daß man das Reaktionsprodukt im Kreislauf führt.

18. Heterogenes Reaktionsverfahren gemäß Anspruch 16, dadurch gekennzeichnet, daß man das Reaktionsprodukt im Kreislauf führt.

20 19. Heterogenes Reaktionsverfahren gemäß Anspruch 13, dadurch gekennzeichnet, daß man das Reaktionsprodukt im Kreislauf führt.

### Revendications

25 1. Procédé pour effectuer une réaction hétérogène, dans lequel un constituant oléosoluble est dispersé dans un constituant hydrosoluble ou dans sa solution aqueuse et est mis à réagir avec le constituant hydrosoluble, caractérisé en ce que le constituant oléosoluble est dispersé en le faisant passer à travers des micropores d'un disperseur fabriqué en une matière hydrophile au fur et à mesure qu'il pénètre dans le constituant hydrosoluble ou dans sa solution aqueuse.

30 2. Procédé de réaction hétérogène suivant la revendication 1, dans lequel le disperseur est fabriqué sous la forme d'une membrane, d'un gel, d'une plaque, d'une autre structure en forme de couche, d'un tissu tissé ou d'un tissu non tissé.

3. Procédé de réaction hétérogène suivant la revendication 1, dans lequel les micropores ont un diamètre de 0,005 à 5 mm.

35 4. Procédé de réaction hétérogène suivant la revendication 3, dans lequel les micropores ont un diamètre de 0,01 à 1 mm.

5. Procédé de réaction hétérogène suivant la revendication 1, dans lequel la matière hydrophile est une matière organique hydrophile, une matière minérale hydrophile, une fibre naturelle ou une fibre artificielle ou synthétique.

40 6. Procédé de réaction hétérogène suivant la revendication 5, dans lequel la matière organique hydrophile est l'alcool polyvinylique, le formol polyvinylique, l'acétalacétique polyvinylique, l'acétal polyvinylique, la cellulose, l'acétyl cellulose, la nitro cellulose, l'acétyl butyl cellulose, l'éthyl cellulose, la méthyl cellulose, la benzyl cellulose, un polypeptide, la gélose, la carragénine ou la gélatine.

45 7. Procédé de réaction hétérogène suivant la revendication 5, dans lequel la matière minérale est le verre, le gypse, le ciment, l'aluminé, un gel de silice ou l'amiante.

8. Procédé de réaction hétérogène suivant la revendication 5, dans lequel la fibre naturelle est le coton, le kapok, le lin, la ramie, le jute, le chanvre de Manille, le sisal, le chanvre de Nouvelle Zélande, la fibre de coco, le mohair, le cachemire, le poil de chèvre, le poil de chameau, la laine de vicogne, le poil d'alpaca, le poil de lama, le crin de cheval ou la soie.

50 9. Procédé de réaction hétérogène suivant la revendication 5, dans lequel la fibre artificielle est la rayonne viscosse, la rayonne cuprammonium, la rayonne polynosique ou la fibre de caséine.

10. Procédé de réaction hétérogène suivant la revendication 1, dans lequel le constituant hydrosoluble est l'eau, l'alcool méthylique, l'alcool éthylique, l'éthylène glycol, le glycérol, le néopentyl polyol, le sucre, le glucose ou le sorbitol.

55 11. Procédé de réaction hétérogène suivant la revendication 1, dans lequel le constituant oléosoluble est un acide carboxylique aliphatique ayant au moins 6 atomes de carbone, un hydrocarbure aliphatique ayant au moins 6 atomes de carbone, un composé aromatique ayant au moins 6 atomes de carbone, des huiles et graisses naturelles animales ou végétales, des glycérides synthétiques, ou un ester.

60 12. Procédé de réaction hétérogène suivant la revendication 11, dans lequel l'ester est l'oléate de méthyle, la palmitate de méthyle, le stéarate d'éthyle, l'oléate d'oléyle, le trioléate de sorbitane ou un ester d'acide gras du saccharose.

65 13. Procédé de réaction hétérogène suivant la revendication 1, dans lequel le constituant hydrosoluble ou sa solution aqueuse et le constituant oléosoluble ont des masses spécifiques suffisamment différentes pour que le constituant oléosoluble monte ou descende à travers le constituant hydrosoluble ou sa solution aqueuse.

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14. Procédé de réaction hétérogène suivant la revendication 13, dans lequel le constituant hydrosoluble ou sa solution aqueuse est contenu dans un récipient et le constituant oléosoluble traverse la matière hydrophile disposée au-dessus ou au fond du récipient.

5 15. Procédé de réaction hétérogène suivant la revendication 13, dans lequel le produit de réaction est un liquide non miscible avec le constituant hydrosoluble ou à sa solution aqueuse, ou y précipite.

16. Procédé de réaction hétérogène suivant la revendication 14, dans lequel le produit de la réaction flotte sur la surface du constituant hydrosoluble ou de sa solution aqueuse.

17. Procédé de réaction hétérogène suivant la revendication 15, dans lequel le produit de la réaction est recyclé.

10 18. Procédé de réaction hétérogène suivant la revendication 16, dans lequel le produit de la réaction est recyclé.

19. Procédé de réaction hétérogène suivant la revendication 13, dans lequel le produit de la réaction est recyclé.

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